

1 Nitrate transport in Chalk catchments-monitoring, modelling and 2 policy implications

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14 **Abstract**

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17 Rising nitrate levels have been observed in UK Chalk catchments in recent decades,
18 with concentrations now approaching or exceeding legislated maximum values in
19 many areas. In response, strategies seeking to contain concentrations through
20 appropriate land management are now in place. However, there is an increasing
21 consensus that Chalk systems, a predominant landscape type over England and indeed
22 northwest Europe, can retard decades of prior nitrate loading within their deep
23 unsaturated zones. Current levels may not fully reflect the long-term impact of
24 present-day practices, and stringent land management controls may not be enough to
25 avert further medium-term rises. This paper discusses these issues in the context of
26 the EU Water Framework Directive, drawing on data from recent experimental work
27 and a new model (INCA-Chalk) that allows the impacts of different land use
28 management practices to be explored. Results strongly imply that timelines for water
29 quality improvement demanded by the Water Framework directive are not realistic for
30 the Chalk, and give an indication of timescales over which improvements might be
31 achieved. However, important unresolved scientific issues remain, and further
32 monitoring and targeted data collection is recommended to reduce prediction
33 uncertainties and allow cost effective strategies for mitigation to be designed and
34 implemented.

35 36 **Introduction**

37 Nitrate is one of the most problematic and widespread of potential groundwater
38 contaminants. It is (indirectly) toxic to humans, as post-ingestion reduction to nitrite
39 causes a form of oxygen starvation that in extreme cases leads to death (Canter,
40 1997). There is also evidence linking nitrate ingestion with increased risk of gastric
41 cancer (Sandor *et al.*, 2001). Livestock, crops and industrial processes can be
42 seriously affected by excessive levels of nitrate in groundwater (Canter, 1997), while
43 elevated nitrate levels in surface water systems have a detrimental impact on river
44 ecology (Hayes and Greene, 1984). Due to these hazards, conservative legislation
45 exists regarding allowable nitrate levels in groundwater and water supplies. Satisfying
46 this legislation is becoming increasingly difficult due to the rising upward trend in
47 nitrate concentrations observed in both surface waters and groundwater over the last
48 decades. Nitrate levels in Cretaceous Chalk aquifers within southern and eastern
49 England are of particular concern, as these aquifers provide 20% of all national water

50 supplies, and up to 60% of the groundwater supply (Downing, 1998). In some
51 systems, concentrations are now hugely above inferred values in pristine conditions;
52 typical baseline nitrate concentrations in UK Chalk groundwaters are thought to be
53 between 2 and 4 mg l⁻¹, with an absolute maximum of 5 mg l⁻¹ (Buss et al, 2005) but
54 concentrations in excess of 50 mg l⁻¹ (the maximum legal limit) have been recorded in
55 Chalk groundwaters since the early 1970's (Foster & Crease, 1974).

56 It is generally accepted that these increases are in main due to intensification of
57 agricultural practices (Foster & Crease, 1974, Limbrick, 2003, Wade *et al.*, 2004).
58 While such a link implies that, with appropriate farm management, a reversal of this
59 trend is possible, there have been increasing concerns regarding the short-to-medium
60 term prognosis of such a reversal in the Chalk. Growing consensus that the Chalk
61 unsaturated zone highly retards a variety of chemicals (Foster, 1993; Mathias *et al.*,
62 2006, Gooddy *et al.*, 2006, Jackson *et al.*, 2007) suggests that much of the historical
63 agricultural loading is still en route to the groundwater within this unsaturated zone. It
64 is likely that this retardation is currently masking the extent of the water quality
65 problem, with negative impacts of present-day practices partially buffered by the less
66 intensive land management earlier within the 20th century.

67

68 This paper discusses the above issues, and explains why conventional water quality
69 models fail to represent adequately the important unsaturated zone processes and the
70 complexity of the groundwater response. Recent work has extended an established
71 catchment-scale nitrogen model (INCA-N, Wade *et al.*, 2002) to provide an
72 appropriate representation of these processes for the Chalk to evaluate nutrient
73 management options (INCA-Chalk, Jackson *et al.*, 2007). Land use management
74 scenario predictions from this model suggest that the timescales demanded by the
75 incoming EU Water Framework Directive are not achievable for many Chalk systems,
76 and provide information on what deadlines and management strategies may be
77 appropriate. However, considerable prediction uncertainties remain due to sparse data,
78 spatial heterogeneity observed in subsurface profiles, and unresolved hypotheses of
79 process response. An evaluation of available data in two Chalk catchments (the Pang
80 and Lambourn, UK) is used to interrogate performance of individual components of
81 the INCA-Chalk model, and suggest where further effort might best be directed to
82 improve understanding and better inform policy.

83

84 **Nitrate legislation in the United Kingdom**

85 The main directives controlling nitrogen levels in water bodies and drinking supplies
86 in the United Kingdom are the European Union Drinking Water Directive
87 (98/83/EEC), Groundwater Directive (80/68/EEC), and the Nitrates Directive. In the
88 UK, the first two apply nationwide, while the Nitrates directive applies only to
89 designated Nitrate Vulnerable Zones (NVZs). These are integrated through the EU
90 Water Framework Directive (WFD) which came into force in December 2000 to
91 expand the scope of water protection to all water bodies: surface water and
92 groundwater; and to achieve 'good' status in all by 2015.

93 The Drinking Water Directive sets guide and maximum admissible concentrations of
94 25 and 50 mg NO₃ l⁻¹ respectively for public supply water; these correspond with the
95 1993 WHO guidelines (DEFRA, 2000). There is already a degree of non-compliance:

96 in 1989, about 1% of the UK population was receiving water with nitrate levels above
97 the maximum legal limit of 50 mg I⁻¹ and over 200 public supply sources exceeded the
98 limit at some time (UK Groundwater Forum, 2004). In other cases, treatment and
99 dilution have been used in order to reduce the concentration in abstracted groundwater
100 before distribution. The economic cost of this is significant (Buss et al, 2005); Dalton
101 and Brand-Hardy (2003) estimated an annual cost to the UK water industry of £16.4
102 million for the period 1992-1997 incurred through treatment alone. Additional
103 expenses are incurred as boreholes with excessive nitrate concentrations are
104 abandoned (Knapp, 2005).

105 The current Groundwater Directive was conceived in a context of point source control
106 of a limited range of substances only (Skinner, 1999), however the WFD provides for
107 the production of a new directive which will go far beyond this. One major advance
108 will be the introduction of regulatory control on diffuse pollution. More generally
109 'good' groundwater status will require that a balance is maintained between
110 abstraction and recharge, the groundwater body does not exhibit effects of saline or
111 other intrusions, does not exceed the Community quality standards and would not
112 result in failure to achieve environmental objectives of associated surface water or
113 terrestrial ecosystems (UK Groundwater Forum, 2004).

114 The Nitrates Directive (91/676/EC) deals explicitly and exclusively with pollution
115 resulting from agricultural activities (direct or indirect). It has a dual objective – the
116 reduction of water 'pollution caused or induced by nitrates from agricultural sources',
117 and 'preventing further such pollution' (Environmental Resources Management,
118 1999). Nitrate polluted waters are identified under the Nitrates Directive as:

- 119 • Surface freshwaters or groundwaters which contain or could contain, if
120 preventative action is not taken, nitrate concentrations greater than 50 mg I⁻¹
121 (11.3 NO₃-N mg I⁻¹).
- 122 • Natural freshwater lakes, or other freshwater bodies, estuaries, coastal waters
123 and marine waters which are eutrophic or may become so in the near future if
124 protective action is not taken.

125 Nitrate Vulnerable Zones (NVZs) are identified as all known areas of land draining
126 into nitrate polluted waters (Osborn & Cook, 1997), which are identified through
127 monitoring data. The Nitrate Directive currently states these designations and
128 associated action programmes should be reviewed on a 4 year cycle. Farmers within
129 these zones are required to adhere to an action programme of measures in order to
130 reduce the amount of nitrate lost from their land to polluted waters. These action
131 programmes are mandatory and uncompensated; DEFRA estimates a net cost to the
132 agricultural industry of £20 million per year and admits that intensive dairy and
133 livestock farmers in NVZs can be particularly economically disadvantaged. The
134 original NVZ designations in 1996 covered 8% of England. Since October 2002 55%
135 of England is categorised as lying within a NVZ and a review of these designations is
136 expected imminently (mid-2007). In April 2006, the Catchment Sensitive Farming
137 Initiative began in forty priority catchments in England. Advisers in these catchments
138 provide dedicated support to farmers, assisting mitigation of diffuse water pollution
139 through promotion of best practice in the use of fertilisers, manures and pesticides,

140 reduced stocking density, maintained or improved soil structure and reduced soil
141 erosion.

142 **Nitrate level predictions in Chalk catchments**

143 Catchment-scale nitrogen models can be broadly classified into metric, conceptual
144 and physics-based models (Wheater *et al.*, 1993). Models in all categories have utility
145 for aspects of nitrogen management (Quinn, 2004; Lacroix *et al.*, 2006); however
146 discussion here is restricted to consideration of their predictive capacity. Metric
147 models are essentially statistical relationships between existing input and output data-
148 sets with rudimentary, if any, physical basis; extrapolation of predictions to conditions
149 for which data has not been collected is generally meaningless and they are not
150 considered further here. Conceptual models involve specifying a model structure *a*
151 *priori*, normally on the basis of a system of conceptual stores (which may be spatially
152 lumped or semi-distributed); where these are derived through simplification of
153 physical processes they are often referred to as “physically-based”. Physics-based
154 fully distributed models seek to capture a system's response by incorporating
155 significant processes through fundamental physical equations. The distinction
156 between physically based semi-distributed conceptual models and fully distributed
157 physics-based models can become blurred depending on the level of simplification
158 and abstraction from reality, spatial resolution, and number of non-measurable or
159 empirical parameters. Strong trade offs also exist between the level of complexity
160 represented and the cost and technical expertise needed for implementation.

161
162 Physics-based distributed nitrogen models at the catchment scale include adaptations of
163 MikeShe (Refsgaard *et al.*, 1999), NPSM (Carruba, 2000) and SHETRAN
164 (Birkinshaw and Ewen, 2000). Particularly complex site specific models also exist
165 (e.g. Wriedt and Rode, 2006). Nitrogen implementations of the well-established
166 SWAT model (e.g. Santhi *et al.*, 2001 and Chu *et al.*, 2004) lie somewhat at the
167 interface between physics-based and conceptual. Fully dynamic conceptual models
168 include SWIM (Krysanova and Becker, 2000), INCA-N (Wade *et al.*, 2002) and
169 HBV-N (Andersson and Arheimer, 2003); other established distributed or conceptual
170 models such as PolFlow (de Wit, 2001), MONERIS (Behrendt *et al.*, 2000),
171 TOPCAT-N (Quinn, 2004), and RIVERSTRAHLER (Billen and Garnier, 2000)
172 include static (time-invariant) and/or metric based representations of important
173 processes and have limited applicability for scenario impact assessments (Andersson
174 *et al.*, 2005). Although it has been contested that the fully distributed physics-based
175 models are most suitable for predictions of the effects of land use changes (Abbot *et*
176 *al.*, 1986), appropriate measurable parameters are rarely obtainable, and extensive
177 calibration is generally required (Beven, 2001). Such calibration can lead to a similar
178 problem to that seen with the metric models: extrapolation to situations not covered
179 by the calibration period is misleading. Although they have great potential for
180 scientific exploration and understanding, the calibration issue and the costs of
181 implementation limit their potential as management tools. As a result, the
182 computationally and parametrically cheaper dynamic conceptual models are
183 increasingly used for predictive modelling (Wade *et al.*, 2004, Andersson *et al.*, 2005,
184 Lacroix *et al.* (2006). These retain the flexibility to represent process response
185 explicitly and to deal with sub-annual time scales (Jackson *et al.*, 2007).
186 Implementation is also less resource-intensive. SWAT, SWIM, INCA-N and HBV-N

187 have been noted specifically as having the level of process description considered
188 most appropriate for general management scenarios (Andersson *et al.*, 2005).
189

190 Although the appropriateness of using such a level of process description for
191 predictive modelling of nitrate levels at catchment scales seems apparent, problems
192 arise when attempting to use current conceptual models to predict the impact of
193 changes in systems such as the Chalk. This is a particularly complex medium,
194 characterised by a fine-pored matrix and the presence of (spatially heterogeneous)
195 fracture networks. Although fractures are the dominant transport pathway within
196 Chalk groundwaters, they are only activated within the unsaturated zone under intense
197 infiltration conditions; indeed flux calculations from experimental data suggest most
198 rainfall events are almost completely accommodated by the Chalk matrix rather than
199 causing fracture flow due to attenuation of infiltrating water within the topsoil
200 (Cooper *et al.*, 1990; Ireson *et al.*, 2006). Water table response is strongly correlated
201 to major infiltration episodes, with a lag time of the order of days to weeks over tens
202 of metres (Headworth, 1972; Ireson *et al.*, 2006). Conversely, contaminants including
203 tritium, nitrate and chlorine migrate slowly downward at rates below 1m per year
204 (Smith *et al.*, 1970; Wellings & Bell, 1980; Oakes *et al.*, 1981; Barraclough *et al.*,
205 1994). Profiles also generally show strong peak preservation consistent with the
206 assumption that matrix flow dominates and dispersion is low (Foster and Smith-
207 Carington, 1980; Geake and Foster, 1989; Mathias *et al.*, 2005), although there are
208 exceptions to this which appear to be correlated to particularly small pore sizes
209 (Geake and Foster, 1989). It is generally assumed that in the deep unsaturated zone
210 and unconfined groundwater, nitrate is effectively conservative (Brouyere *et al.*, 2004;
211 Price *et al.*, 1993), although there is some evidence that this is not true under some
212 geochemical conditions (Buss *et al.*, 2005) and further research on this is required. It
213 has historically been difficult to reconcile the rapid response of the water table with
214 the absence of fracture flow and slow contaminant migration rates due to the
215 limitations in hydraulic conductivity and storage within the Chalk under specific
216 pressure conditions. Headworth (1972) interpreted the recharge mechanism as a
217 system of displacement, with “new water” entering the top of the partially saturated
218 Chalk displacing a similar quantity of “old water” at the bottom. This explanation is
219 now well-supported by both experimental and modelling studies (Brouyere *et al.*,
220 2004, Mathias *et al.*, 2006, Brouyere, 2006, Ireson *et al.*, 2006).

221
222 The depths within the Chalk unsaturated zone vary significantly over both space and
223 time, dependant on distance from rivers and streams and on season; but are typically
224 of the order of tens of metres. Interfluvial values approaching one hundred metres are
225 not uncommon, see for example the depth distribution of the Lambourn catchment
226 (Figure 1). As a result of the slow travel times and the spatial variation in vertical
227 distance of the unsaturated zones, water exiting from the unsaturated zone is of
228 varying age, with a corresponding mixed history of nutrient loading. Adequate
229 representation in models of both this distribution of travel times and the contrasting
230 slow nutrient/ fast water table response is necessary for meaningful consideration of
231 the implications of previous loadings on future concentrations, and to allow estimates
232 of the time-scales over which future changes in land use change might impact
233 (Jackson *et al.*, 2006). Representing such effects in fully distributed physics-based
234 models, where pressure and gravity drive water transport, is possible (although
235 difficult to calibrate appropriately). However, conceptual models, typically consisting

236 of a limited number of linear stores which act as “buckets” releasing water, are unable
237 to represent both the fast water response and the slow chemical transport in an
238 integrated manner. Accordingly, Jackson *et al.* (2006) draw on insights from data and
239 the physically based modelling described in Mathias *et al.* (2006) to present a simple
240 methodology for representing the unsaturated zone, appropriate for large scale
241 models. To account for the different periods over which responses occur, transport of
242 solute and water is treated separately within the unsaturated zone and combined at the
243 water table. The history of application is accounted for through routing solutes
244 through a distribution of travel times, obtained through combining digital elevation
245 and groundwater maps and scaling the resultant distribution of unsaturated zone
246 depths by the rate of average vertical nitrate movement. The approach is both
247 consistent with current understanding of the dominant processes, and simple to
248 implement within most catchment scale hydrological models. The only significant
249 modifications required are the addition of a single difference equation and storage of
250 the history of soil concentrations accumulated as a simulation progresses (see Jackson
251 *et al.*, 2006 for a full description of the algorithm). It is also parsimonious; assuming
252 digital elevation data and sufficient information on groundwater levels is available,
253 only one additional parameter (travel time within the unsaturated zone) is required.
254 Although it might initially seem reasonable to relate this rate of movement to
255 hydrologically effective rainfall and rock porosity rather than defining it directly, such
256 an approach is not appropriate in the Chalk, due to its fine-pored matrix which drains
257 negligibly under typical field pressure conditions. It is better characterised through
258 data from the isotope and other tracer studies described previously.

259
260 A well-established semi-distributed catchment-scale model of nitrogen (INCA-N,
261 described in Wade *et al.*, 2002) was extended to include this representation. The
262 revised model (INCA-Chalk) takes account of the retardation caused by the
263 unsaturated zone in addition to the biogeochemical transformations and spatially
264 distributed hydrological routing included within the original INCA model. Jackson *et al.*
265 (2007) used this model to examine historical and predict future nitrate
266 concentrations under different land management scenarios using existing and
267 projected data within a predominantly agricultural Chalk catchment in Southern
268 England (the Lambourn). This and an adjacent catchment (the Pang) have been a
269 focus for extensive multi-disciplinary research within the UK (Neal *et al.*, 2004b;
270 Wheeler and Neal, 2006). Sixteen subcatchments, with six land use types, were
271 considered. A travel time of 1m year⁻¹ was assumed, and fifty pathways used to
272 represent the unsaturated zone depth distribution (corresponding exactly to that
273 presented in Figure 1); note this implies that, given constant agricultural inputs, over
274 80 years are needed to reach anything close to an equilibrium level within
275 groundwater and rivers.

276 Despite the relative wealth of available data due to the research focus on this
277 catchment, obtaining reliable historical land use and fertiliser application data was
278 problematic. National land use records and livestock numbers are based on
279 infrequently collected census data; only six sets of data are available over the last 100
280 years and periods where rapid land use changes occurred are often not covered (e.g.
281 around the 1939-1945 war). Spatial resolution is also poor, with public domain data
282 averaged over large areas (2km or more) due to privacy laws. Information on fertiliser
283 application rates does not even extend to this level of resolution. In the absence of
284 catchment-specific information, fertiliser application rates for each period and for
285 each of the six land uses for all sixteen subcatchments were taken from Johnes *et al.*

286 (1998), where application rates are differentiated by geo-climatic region. The timing
287 of the fertiliser applications was assumed to be the same as those observed in a survey
288 of fertiliser practice from the River Ant (Johnes *et al.*, 2003). Under these
289 assumptions, the derived current-day annual nitrogen inputs from fertiliser for both
290 cereal and other arable land uses were approximately constant for each sub-catchment
291 at $175 \text{ kg N ha}^{-1} \text{ year}^{-1}$, while subcatchment input rates to ‘grassland’ varied between
292 90 and $170 \text{ kg N ha}^{-1} \text{ year}^{-1}$ depending on the ratio of permanent and temporary
293 grassland, and rough grazing (Wade *et al.*, 2006). Inputs from livestock were highly
294 variable between subcatchments, between 60 and $350 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Table 1
295 presents available census dates, along with associated proportions of the two
296 dominant land use classes within the Lambourn (arable and grassland), and
297 catchment-averaged agricultural inputs shown as a proportion of current-day
298 application rates. The majority of the census data is applied from the beginning of the
299 year it is collected until the end of the year previous to the next collection. To account
300 for post-war increase in fertiliser use, the census data from 1931 is used from the start
301 of the period of interest, 1920, until the end of 1944. The 1969 census data is then
302 applied to 1945-1975, the post-war period. The model was calibrated over the entire
303 period of available data (1920 to 2003) using the Monte Carlo procedures presented in
304 McIntyre *et al.* (2005) and least squares measures of fit; the resultant parameterisation
305 provides a visually excellent fit to available flow and nitrate concentration data (see
306 Jackson *et al.*, 2007). To examine the time-scales over which effects from land
307 management changes might take place, two fertiliser application scenarios were
308 considered, the first with current-day practices continuing until 2100, and the second
309 with all agricultural nitrate loading cut from 2003. Further details of the model setup
310 and data used are in Jackson *et al.* (2007); note that projected data utilises
311 B2HADCM3; a relatively conservative climate change scenario assuming slow
312 population growth and technological advances moderating human emissions.

313
314 Figure 2 shows groundwater and in-river nitrate concentrations in the Lambourn
315 under the two nutrient loading scenarios; note that the simulation with future loading
316 cut to zero, which can be considered a “better than best case” scenario, has serious
317 implications for the timescale over which improvements in groundwater quality can
318 reasonably be expected, and hence for compliance with the EU Water Framework
319 Directive. Reversal in the in-river nitrate concentration trend is not appreciable until
320 around 2040, while the groundwater problem is even more severe, with significant
321 decreases not occurring until past 2060. This suggests that historical loading of
322 catchments such as the Lambourn will dominate groundwater quality decades into the
323 future, and its impacts must be considered in any predictions and corresponding
324 policy decisions. The implications of doing nothing are much worse; if current
325 nitrogen loading levels continue a steady increase in both mean in-river and
326 groundwater concentrations can be expected for most of the remainder of the century.
327 The implications of the above results for policy are of great concern, as they suggest
328 that increasing trends in nitrate concentrations in groundwater sources may be
329 impossible to reverse through land management alone in the next few years, and that
330 achievement of ‘good’ chemical status by 2015, as required by the Water Framework
331 Directive, may not be feasible. There is minimal flexibility in nitrate legislation where
332 drinking water is concerned; it is probable that reduction of nitrate levels via
333 groundwater treatment will be increasingly necessary. This may require considerable
334 investment in technology, as current methods for reducing nitrate concentrations are
335 expensive and difficult to implement on large scales (Canter, 1997). In-situ biological

336 denitrification, induced either through the injection of a carbon source (Tomkins *et*
337 *al.*, 2001) or through constructed wetlands to remove nitrate (Prior and Johnes, 2002),
338 is particularly desirable as infrastructure costs are likely to be reduced and the
339 potential exists to satisfy ecological as well as drinking supply purposes. For either of
340 these to be effective, some knowledge on appropriate placement within a catchment is
341 required; implementation of any in-situ system in a position by-passed by the great
342 majority of water would have negligible effect regardless of its efficiency at the site
343 itself.

344 Where water is not taken directly for human consumption, more flexibility exists:
345 there is provision for setting less stringent objectives for specific water bodies where
346 it would be unfeasibly or disproportionately expensive to achieve 'good' status (due
347 to human activity or otherwise), and the 2015 target date can be extended where there
348 are reasonable grounds (UK Groundwater Forum, 2004). To establish what targets
349 might be reasonable will however require considerable further work. Although INCA-
350 Chalk has been shown to be capable of good reproduction of observed in-river nitrate
351 concentrations, and some confidence in the overall system analysis appears
352 reasonable, considerable prediction uncertainties remain due to sparse data, spatial
353 heterogeneity, and unresolved hypotheses of process response. It is possible that
354 components of the model where limited or no data have been available for calibration
355 possess compensatory errors; indeed Wade *et al.* (2006) note an equifinality problem
356 in the Lambourn catchment, with data insufficient to determine the relative
357 contribution of subsurface or in-river nitrate losses or transformations. It is therefore
358 strongly recommended that further work to discriminate between differing process
359 hypotheses is carried out to improve the predictive capabilities of models such as
360 INCA-Chalk. To provide preliminary guidance on this, we now use an evaluation of
361 subsurface data in two Chalk catchments within the United Kingdom (the Pang and
362 Lambourn) to interrogate individual components of the Chalk system response, and
363 suggest where further effort might best be directed to improve understanding and
364 better inform policy.

365

366 **Subsurface data on nitrates in the Chalk**

367 Data from the Pang and Lambourn catchments were obtained and an analysis of solute
368 profile data, land use data, fertiliser application data, groundwater level data and
369 climate data performed. Correlations between features in solute profiles and other data
370 sets were investigated with a view to establishing the source of solute peaks and other
371 characteristics. Recent porewater chemistry profiles collected as part of the LOCAR
372 research initiative described in Wheater and Peach (2004) and Wheater *et al.* (2007)
373 were available from a number of boreholes at five sites located within the Pang and
374 Lambourn catchments (Adams *et al.*, 2003). In addition, a selection of profiles from
375 British Geological Survey (BGS) borehole monitoring during the late 1980s at an
376 additional seven sites within the Pang/Lambourn area was acquired. TON (Total
377 Oxidisable Nitrogen) and NO₃-N data were considered in the context of the hydrology
378 and geology of the area. Difficulties in obtaining agricultural loading data at the
379 catchment scale have already been noted. Attempts to obtain detailed records from
380 specific sites were only partially successful, although some application records and
381 land use information were kindly provided by managers of the land containing the
382 LOCAR boreholes, allowing associated solute profiles to be analysed in the context of
383 localised land use and N applications. Farms within NVZs are now required to hold

384 fertiliser application data for 5 years, however more generally few farmers have kept
385 written records of land use or fertiliser applications and tacit knowledge disappears
386 with time and when changes in land ownership occur. Without such data, it is difficult
387 to define trends in application inputs, and extremes or localised effects cannot be
388 identified. These effects can be significant: although data from Geake and Foster
389 (1989) and predictions from the leaching model SUNDIAL (Goulding *et al.*, 1998),
390 suggest that *average* annual leaching losses below Chalk are close to half the rate of
391 nitrogen fertiliser application, differences in soil management methods (e.g. drainage,
392 cultivation systems, rotations, type of fertilizer/sludge applied) cause significant
393 deviations from this at any specific location (Dowdell and Mian, 1982). Andrews *et*
394 *al.* (1997) demonstrate a significant link between application methodology and rate of
395 nitrate leaching from topsoil to Chalk; data also shows the most substantial peaks
396 being associated with large sludge applications and ploughing of grass crops.
397 Addiscott (1996) also notes the potential contribution of ploughing to large nitrate
398 peaks within the Chalk based on cores taken twenty years after the ploughing of old
399 permanent grassland.

400 The porewater TON profiles from each of the five LOCAR sites (presented in Figure
401 3) indicate that significant variation can exist in TON concentration with depth, with
402 the largest variations occurring within the unsaturated zone. Large peaks in TON
403 concentration were present at three sites; PL10A, PL13A and PL26 at around 17 m,
404 25 m and 10 m respectively. These peaks were all within the unsaturated zone,
405 according to water table locations taken at the time of drilling. Borehole PL11 was
406 located near the river and hence the profile was, in the main, located within the
407 saturated zone. Low TON concentrations exist throughout this profile, with only
408 relatively small variations. Borehole PL14 is located near the interfluvium, and the entire
409 core was within the unsaturated zone at the time of drilling. All profiles exhibited
410 lower TON concentrations in the saturated zone. This is in agreement with current
411 understanding and is presumed to be, in general, due to groundwater mixing, dilution
412 and dispersion. If oxygen is limited in this saturated region (this is currently
413 unknown), the reduction of NO₃-N to N₂ via denitrification may also contribute. At
414 present, TON concentrations within the saturated zone in all boreholes are within the
415 nitrate level limit set by the Water Framework Directive (11.3 mg l⁻¹ N, which
416 corresponds to 50 mg l⁻¹ of nitrate).

417 The origin of the LOCAR data peaks within the unsaturated zone are unknown,
418 however examination of soil moisture deficit time series led to speculation that the
419 peaks could be related to high recharge events coinciding with nitrate applications.
420 Lithological information provided an explanation for the low concentrations observed
421 within PL14. Unlike the other sites, where chalk was predominately present within the
422 entire profile, the chalk in PL14 was overlain by 33 metres of Palaeogene deposits.
423 The low concentrations observed in this profile are almost certainly due to a
424 significant reduction in nitrate leaching into the subsurface due to these relatively
425 impermeable deposits. Considering peaks, the lithological borehole logs for PL26
426 showed 'putty' chalk near the zone of increased concentration, with a band between
427 4.5m and 5.5m, and some localised 'putty' chalk around 9.5 m -10.1 m (more
428 generally Seaford Chalk was present from the surface to a depth of around 67m). It
429 may be possible that the 'putty' chalk retards flow and thus solute accumulates
430 locally. However, no previous association between putty chalk and high
431 concentrations is known, and it seems unlikely that this would cause such a significant

432 increase as that evident from the TON profile. Unfortunately lithological information
433 was not available for sites PL10A and PL13A and thus a comparison between
434 geological features and TON concentration could not be carried out for these sites.

435 Data from non-LOCAR sites is also illuminating; showing large spatial variability
436 within profiles within a few hundred metres of each other and with similar histories of
437 fertiliser applications. Figure 4 shows NO₃-N profiles obtained from four boreholes to
438 21m depth at one site within the Lambourn during the winter of 1988/1999. The water
439 table depth at this site is between 30 m and 40 m below ground level; hence all
440 profiles are fully within the unsaturated zone. Boreholes BE01A and BE02A are
441 located in land with a history of permanent pasture for more than 25 years previous to
442 sampling, while boreholes BE03A and BE04A are located in land that has been under
443 permanent pasture since 1981 and possessed a kale crop during 1979 and 1980. The
444 land use prior to this is unknown. At all four sites, the history of nitrogen fertiliser
445 applications is 166 kg ha⁻¹ yr⁻¹ (nitrogen) from 1979-1989. All profiles show
446 extremely high NO₃-N concentrations at some point, but peak depths between the
447 profiles do not correspond, either with ordnance datum elevation or depth below
448 ground level. Given the close proximity of the boreholes and their similar land use
449 histories, these differences do not appear to be due to changes in meteorological or
450 cropping conditions. The differences may be caused by a variation in soil types or
451 very local scale agricultural effects (e.g. stock preferences for particular locations,
452 impacts of drainage or farm machinery); it is also possible that there is a geological
453 explanation. Variation in peak depths has important implications for predictive
454 scenarios.

455 A pressing question given the ambiguities present in the above data is to what degree
456 models like INCA-Chalk can represent nitrate leaching to the unsaturated zone at any
457 particular point in the catchment. Direct comparisons were difficult, due to the very
458 sparse fertiliser input data available. Nitrate profiles from INCA-Chalk (derived
459 through taking the nitrate mass entering the unsaturated zone from the soil and
460 assuming a travel time of 1m per year), for both grassland and cereal, are shown in
461 Figure 5. However model outputs and experimental data were not comparable,
462 perhaps in average magnitude but certainly not in form; the INCA-Chalk profiles had
463 clearly defined annual peaks present in most years along with substantial intra-annual
464 variability, although the magnitude of these peaks vary according to atmospheric
465 conditions around the time of fertiliser applications. The discrepancy may be in main
466 due to poor nutrient loading data quality but also raises questions as to the adequacy
467 of current soil representations for systems such as the Chalk. INCA-Chalk follows
468 the hydrological representation of INCA-N (Wade *et al.*, 2002), a classic hydrological
469 conceptualisation in which contributions from the soil component are partitioned
470 between the deeper subsurface (percolation) and the river (through-flow) using a
471 baseflow index. Hence concentrations entering the deeper subsurface and exiting to
472 the river are equal at any one time. Data does not necessarily support this assumption.
473 Soil concentrations near the surface are very variable due to biogeochemical
474 influences and temporal variation in surface applications (e.g. fertilisers and
475 atmospheric deposition), and the effect of this is seen in in-river concentration data.
476 However most of the variation observed in deeper subsurface data appears to be a
477 consequence of changes over longer time periods; there is little obvious seasonal
478 variation. This may partially be an artefact of the sampling process, which necessarily
479 integrates water taken over tens of centimetres within each discrete measurement;

480 however a smoothing effect on concentrations in the deeper part of the soil would be
481 consistent with the advection dispersion processes governing the transport of nitrate in
482 soils. Some form of differentiation between the two output concentrations may be
483 required to improve subsurface representation. However, experimental data
484 examining variations in nitrogen transport and speciation with depth in Chalk soils
485 and associated physically based modelling studies would be required to achieve this
486 satisfactorily.

487 Although it is evident that the soil exerts a strong control on nitrate levels in the
488 Chalk, there are also questions regarding a “deeper” subsurface effect; i.e. that caused
489 by variations in water table level within the Chalk aquifer. Analysis of groundwater
490 level data in the Pang and Lambourn over a thirty year period showed groundwater
491 heads to vary significantly within the catchment, with strong seasonal fluctuations but
492 also substantial intra-annual variability. Figure 6 presents three example timeseries.
493 Groundwater heads generally increase with distance from the river, as well as distance
494 upstream within the catchment. Fluctuations tend to be small close to the river, and
495 large close to the interfluvium, although small fluctuation magnitudes also exist close to
496 dry valleys and tributaries, perhaps due to increased permeability, or in some cases,
497 impeding layers. In locations towards the interfluvium, fluctuations of over 35m were
498 observed; this is consistent with data from other Chalk catchments where fluctuations
499 as great as 40m have been noted (Price *et al.*, 1993). As the effective aquifer is
500 generally only the upper 50-60 m of saturated chalk due to a decrease in permeability
501 with depth (Price *et al.*, 1993), this “seasonally unsaturated zone” can be a significant
502 component of the total aquifer thickness. It has been shown by examination of the
503 effect of fluctuating water table on solute concentrations in mobile fissures and solute
504 distribution in matrix pore-water that the scale of water table fluctuations can be the
505 dominant control on solute concentration in mobile groundwater (Fretwell *et al.*,
506 2000). At two of the three cores containing the high peaks, nearby groundwater levels
507 were spatially similar and temporal water table variations (around 8m near PL26 and
508 13m near PL13) were superimposed. Both showed some indication that a decrease in
509 concentration is occurring with depth over this range of fluctuation. It is important to
510 establish whether the effects of this fluctuating region on solute transfer have
511 significant consequences for future timescales of trend reversal or absolute
512 magnitudes of concentrations reached.

513 While the causes of the distinct peaks in the obtained profiles could not be
514 satisfactorily resolved given data limitations, it is clear that they will result in an
515 increase of nutrient input to groundwater some time in the future. It is unclear how
516 large an impact this will have on overall groundwater concentration, due to unknown
517 spatial variability as well as the possibility of diffusion in the seasonally unsaturated
518 zone which may attenuate the effects. In order to better explore the causes and long
519 term effects of solute profile peaks and other characteristics, a long record of historic
520 land use and nitrate applications is desired in addition to climatic data such as
521 precipitation and soil moisture deficit and detailed geological data.

522 **Conclusions**

523 More than half of UK groundwater supplies are abstracted from the Chalk aquifers of
524 eastern and southern England, many of which are becoming nitrate polluted as a
525 consequence of UK agricultural practices. While changes in land use management are
526 arguably the most effective long term means of controlling this, there are well-

527 founded concerns that the unsaturated zone in lowland Chalk will prevent control of
528 nitrogen levels being achieved within the timescales demanded by incoming European
529 and UK legislation. Chalk catchments, in the UK and elsewhere in Europe, will
530 require detailed assessment to confirm whether they will be in breach of the EU Water
531 Framework Directive's target for "good" status by 2015 and well beyond, and assess
532 the timescales in which "good" status may be achievable. Until very recently, no
533 catchment-scale models capable of treating the complexities of the Chalk were
534 available; a suitable management tool has only recently been developed.

535 Although this represents a significant advance in predictive capabilities of nitrates in
536 Chalk systems, INCA-Chalk or subsequent models require further data support and
537 refinement to better inform strategies to contain nitrate pollution. Key areas for
538 further work include improving the spatio-temporal resolution of nutrient loading
539 input data and information on topsoil nitrogen speciation and leaching, as well as the
540 representation of diffusion in the seasonally unsaturated zone. Collection of spatially
541 representative porewater and groundwater nitrate concentration samples to allow
542 further subsurface calibration would also reduce the equifinality problem outlined in
543 Wade *et al.* (2006). It is clear that although INCA-Chalk provides an effective tool for
544 catchment-scale simulation, an improved understanding of nitrogen movement
545 through the soil-unsaturated chalk-groundwater continuum (through targeted studies
546 examining nitrogen transport and transformations within Chalk topsoils, further
547 subsurface data analysis and process modelling) is required before further notable
548 progress in nitrate modelling of Chalk catchments can be achieved.

549

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551

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562 505540).

References

- Abbot, M.B., Bathurst, J.C., Cunge, J.A., O'Connell, P.E., Rasmussen, J., 1986. An introduction to the European Hydrological System - Systeme Hydrologique Europeen, "SHE", 1: History and philosophy of a physically-based, distributed modelling system. *J. Hydrol.* 87, 45-59.
- Adams, B., Peach, D.W., Bloomfield, J.P., 2003. The LOCAR Hydrogeological Infrastructure for the Pang/Lambourn Catchment. British Geological Survey Internal Report, IR/03/178, available from BGS, Keyworth, Nottingham, UK.
- Addiscott, T., 1996. Fertilisers and nitrate leaching. *Issues Envir. Sci.* 5, 1-26.
- Andersson, L., Arheimer, B., 2003. Modelling of human and climatic impact on nitrogen load in a Swedish river 1885-1994. *Hydrobiologia* 497, 63-77.
- Andersson, L., Rosberg, J., Pers, B.C., Olsson, J., Arheimer, B., 2005. Estimating Catchment Nutrient Flow with the HBV-NP Model: Sensitivity To Input Data. *Ambio* 34(7), 521-532.
- Andrews, R. J., Lloyd, J. W., Lerner, D. N., 1997. Modelling of nitrate leaching from arable land into unsaturated soil and chalk 2. Model confirmation and application to agricultural and sewage sludge management,. *J. Hydrol.* 200, 198-221.
- Beven, K., 2001. The Dalton lecture: how far can we go in distributed hydrological modeling? *Hydrol. Earth Syst. Sci.* 5, 1-12.
- Barraclough, D., Gardner, C.M.K., Wellings, S.R., Cooper, J.D., 1994. A tracer investigation into the importance of fissure flow in the unsaturated zone of the British Upper Chalk. *J. Hydrol.* 156, 459-469.
- Behrendt, H., Huber, P., Kornmilch, M., Optiz, D., Schmoll, O., Scholz G., Ueber, G., 2000. Nutrient balances of German river basins. UBA-Texte 23/2000, 261pp.
- Billen G., Garnier J., 2000. Nitrogen transfers through the Seine drainage network: a budget based on the application of the Riverstrahler model. *Hydrobiologia* 410, 139-150.
- Birkinshaw, S. J. and Ewen, J., 2000. Nitrogen transformation component for SHETRAN catchment nitrate transport modelling. *J. Hydrol* 230, 1-17.
- Brouyere, S., Dassargues, A., Hallet, V., 2004. Migration of contaminants through the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. *J. Contam. Hydrol.* 72, 135-164.
- Brouyere, S, 2006. Modelling the migration of contaminants through variably saturated dual porosity, dual permeability chalk. *J. Contam. Hydrol.* 82(4), 195-219.

Buss, S.R., Rivett, M.O., Morgan., P., Bemment, C.D., 2005. Attenuation of nitrate in the sub-surface environment. Environment Agency of England and Wales Science Report SCO30155/SR2.

Canter, L.W., 1997. Nitrates in Groundwater. CRC Press, USA.

Carrubba, L., 2000. Hydrologic Modeling at the Watershed Scale Using NPSM. J. Amer. Water Resour. Assoc. 36, 1237-1246.

Chu, T.W., Shirmohammadi, A., Montas, H., Sadeghi, A., 2004. Evaluation of the SWAT model's sediment and nutrient components in the Piedmont Physiographic Region of Maryland. Trans. ASAE 47(5), 1523-1538.

Cooper, J.D., Gardner, C.M.K., MacKensie, N., 1990. Soil water controls on recharge to aquifers. J. Soil Sci. 41, 613-630.

Dalton, H, Brand-Hardy, R., 2003. Nitrogen- the essential public enemy. J. App. Ecol. 40, 771-781.

de Wit, M., 2001. Nutrients fluxes at the river basin scale. I: the PolFlow model. Hydrological Processes 15, 743-759.

Department of the Environment, Food & Rural Affairs (DEFRA), 2000. The Water Supply (Water Quality) Regulations 2000. S.I. 2000 No. 3184.

Dowdell, R. J., Mian, M. H., 1982. Fate of nitrogen applied to agricultural crops with particular reference to denitrification. Phil. Trans. Roy. Soc. Lon. B., 363-373.

Downing R. A., 1998. Groundwater: our Hidden Asset. British Geological Survey, available from BGS, Keyworth, Nottingham, UK.

Environmental Resources Management, 1999. Verification of Vulnerable Zones Identified Under the Nitrate Directive and Sensitive Areas Identified Under the Urban Waste Water Treatment Directive. UK. European Commission Directorate General.

Foster, S. S. D., 1993. The Chalk aquifer- its vulnerability to pollution, in The Hydrogeology of the Chalk of North-West Europe. In R. A. Downing, M. Price, G. P. Jones (ed). Clarendon Press, Oxford, pp1-13.

Foster, S.S.D, Crease, R.I., 1974. Nitrate pollution of Chalk groundwater in East Yorkshire – a hydrogeological appraisal. J. Instit. Wat. Eng. 28, 178-194.

Foster, S. S. D, Smith-Carington, A. 1980. The interpretation of tritium in the Chalk unsaturated zone. J. Hydrol. 46, 343-364.

Fretwell, B.A., Burgess, W., Barker, J.A., 2000. Contaminant retardation within the seasonally unsaturated zone of the Chalk aquifer: the SUZ process. In: Dassargues, A. (ed). Tracers and modelling in Hydrogeology. IAHS Press, Wallingford, pp. 385-390.

- Geake, A.K., Foster, S.D., 1989. Sequential isotope and solute profiling in the unsaturated zone of British Chalk. *Hyd. Sci. J.* 34, 79-95.
- Goody, D. C. W, Darling, G., Shand, P., Abesser, C., 2006. Using Chlorofluorocarbons (CFCs) & Sulphur Hexafluoride (SF6) to characterise groundwater movement and residence time in a lowland Chalk catchment. *J. Hydrol.* 330(1-2), 44-52.
- Goulding, K.W.T., Bailey, N. J., Bradbury, N. J., 1998. A modelling study of nitrogen deposited to arable land from the atmosphere and its contribution to nitrate leaching, *Soil Use Manag.* 14, 70-77.
- Hayes, C.R., Greene, L. A., 1984. The evaluation of eutrophication impact in public water supply reservoirs in East Anglia. *Wat. Poll. Contr.* 83, 45-51.
- Headworth, H.G., 1972. The analysis of natural groundwater level fluctuations in the Chalk of Hampshire. *J. Instit. of Wat. Eng.* 26, 107-124.
- Ireson, A., Wheeler, H.S., Butler, A.P., Mathias, S.A., Finch, J., Cooper, J.D., 2006. Hydrological processes in the Chalk unsaturated zone- insights from an intensive field monitoring programme. *J. Hydrol.* 330, 29-43.
- Jackson, B.M., Wheeler, H.S., Mathias, S.A., McIntyre, N., Butler, A.P., 2006. A simple model of variable residence time flow and nutrient transport in the Chalk, *J. Hydrol.* 330, 221-234.
- Jackson, B.M., Wheeler, H.S., Wade, A.J., Butterfield, D., Mathias, S.A., Ireson, A.M., Butler, A.P., McIntyre, N.R., Whitehead, P.G., 2007. Catchment-scale modelling of flow and nutrient transport in the Chalk unsaturated zone. *Ecol.Model.* (2007), doi:10.1016/j.ecolmodel.2007.07.005.
- Johnes, P.J., Bennion, H., Curtis, C., Moss, B., Whitehead, P., Patrick, S., 1998. Trial Classification of Lake Water Quality in England and Wales. Report from Environment Agency Project E2-i721, Environment Agency, Bristol, p. 264.
- Johnes, P.J., Whitehead, P.G, Davies, S., Wade, A.J., Butterfield, D., 2003. Effectiveness of Eutrophication Control by Phosphorus Reduction. Environment Agency R&D Technical Report, Bristol, 149pp
- Knapp, M. F., 2005. Diffuse pollution threats to groundwater: a UK water company perspective. *Quat. J. Eng. Geol. Hydr.* 38, 39-51.
- Krysanova, V. and Becker, A., 2000. Integrated modeling of hydrological processes and nutrient dynamics at the river basin scale. *Hydrobiologia* 410, 131–138.
- Lacroix, A., Laurent, F., Ruelland, D., Sauboua, E., 2006. Nitrate pollution risk assessment: from the model to the indicator, *Intern. J. Agric. Resour.Gov. Ecol.* 5, 206–223.

- Limbrick, K.J., 2003. Baseline nitrate concentration in groundwater of the Chalk in south Dorset, UK. *Sci. Tot. Envir.* 314-316, 89-98.
- Mathias, S.A., Butler, A.P., McIntyre, N., Wheater, H.S., 2005. The significance of flow in the matrix of the Chalk unsaturated zone, *Journal of Hydrology*, 310, 62 - 77.
- Mathias, S.A., Butler, A.P., Jackson, B.M., Wheater, H.S., 2006. Transient simulations of flow and transport in the Chalk unsaturated zone. *J. Hydrol.* 330, 10-28.
- McIntyre, N., Jackson, B.M., Wade, A.J., Butterfield, D., Wheater, H.S., 2005. Sensitivity analysis of a catchment-scale nitrogen model. *J Hydrol.* 315, 71 – 92.
- Neal, C., Jarvie, H. P., Wade, A. J., Neal, M., Wyatt, R., Turner, H., Hill, L., Hewitt, N., 2004. The water quality of the LOCAR Pang and Lambourn catchments. *Hydrol. Earth Sys. Sciences* 8, 614–635.
- Oakes, D.B., Young, C.P., Foster, S.S.D, 1981. The effects of farming practices on groundwater quality in the United Kingdom. *Sci. Tot. Env.* 21, 17-30.
- Osborn, S., Cook, H.F., 1997. Nitrate Vulnerable Zones and Nitrate Sensitive Areas: A policy and technical analysis of groundwater source protection in England and Wales. *J. Envir. Plan. Manag.* 40(2), 217-233.
- Price, M., Downing, R. A., W. M. Edmunds, 1993. The Chalk as an aquifer. In: *The Hydrogeology of the Chalk of north-west Europe*, Downing R.A., Price M. and G.P. Jones (eds.), Clarendon Press, Oxford, pp. 35-58.
- Prior, H., Johnes, P. J., 2002. Regulation of surface water quality in a Chalk catchment, UK: an assessment of the relative importance of instream and wetland processes. *Sci. Tot. Env.* 282/283, 159-174.
- Quinn, P. 2004. Scale appropriate modeling: representing cause-and-effect relationships in nitrate pollution at the catchment scale for the purpose of catchments scale planning. *J. Hydrol.* 291, 197–217.
- Refsgaard, J.C., Thorsen, M., Jensen, J.B., Kleeschulte, S., Hansen, S., 1999. Large scale modeling of groundwater contamination from nitrate leaching. *J. Hydrol.* 221, 117-140.
- Santhi, C., Arnold, J.G., Williams, J.R., Dugas, W.A., Hauck, L., 2001. Validation of the SWAT model on a large river basin with point and nonpoint sources. *Tech Publ. Ser. Am. Water Resour. Assoc.* 37, 1169–1188.
- Sandor, J., Kiss, I., Farkas, O., Ember, I., 2001. Association between gastric cancer mortality and nitrate content of drinking water: Ecological study on small area inequalities. *Eur. J. Epidem.* 17, 443-447.

- Skinner, A., 1999. Groundwater Protection – an Overview of Current Issues, Proceedings of the Seminar “Groundwater Protection in Ireland”, Enniskillen, 8 October 1999.
- Smith, D.B., Wearn, P.L., Richards, H.J., Rowe, P.C., 1970. Water movement in the unsaturated zone of high and low permeability strata using natural tritium. In: Isotope Hydrology, pp.73-87. Atomic Energy Agency, Vienna.
- Tompkins, J. A., Smith, S. R., Cartmell, E., Wheater, H. S., 2001. In-situ bioremediation is a viable option for denitrification of Chalk groundwaters. *Quat. J. of Eng. Geol. Hydr.* 34, 111-125.
- UK Groundwater Forum, 2004. Nitrate and pesticide pollution, British Geological Survey publication IPR/47-4, available from BGS, Keyworth, Nottingham, UK.
- Wade, A. J., Butterfield, D., Whitehead, P. G., 2006. Towards an improved understanding of the nitrate dynamics in lowland, permeable river-systems: Applications of INCA-N. *J. Hydrol.* 330, 185-203.
- Wade, A.J., Durand, P., Beaujouan, V., Wessel, W.W., Raat, K.J., Whitehead, P.G., Butterfield, D., Rankinen, K., Lepisto, A., 2002. A nitrogen model for European catchments: INCA, new model structure and equations. *Hydrol. Earth Syst. Sci.* 6(3), 559-582.
- Wade, A. J., Whitehead, P.G., Jarvie, H. P., Neal, C., Prior, H., Johnes, P. J., 2004. Nutrient monitoring, simulation and management within a major lowland UK river system: the Kennet. *Math. Comp. Sim.* 64, 307-317.
- Wellings, S.R., Bell, J.P., 1980. Movement of water and nitrate in the unsaturated zone of the upper Chalk near Winchester, Hants, England. *J.Hydrol.* 48, 119-136.
- Wheater, H. S., Neal, C. (eds), 2006. Hydro-ecological functioning of the Pang and Lambourn catchments, UK: Results from the LOWland CATCHment Research (LOCAR) initiative, special issue of *J. Hydrol.* 330(1-2).
- Wheater, H.S., Peach, D, 2004. Developing interdisciplinary science for integrated catchment management: the UK LOWland CATCHment Research (LOCAR) programme. *Intern. J. Water Resour. Devel.* 20, 369-385.
- Wheater, H.S., Jakeman, A.J., Beven, K.J., 1993. Progress and Directions in Rainfall-runoff Modelling, in *Modelling Change in Environmental Systems*, edited by Jakeman, A.J., Beck, M.B, McAleer, M.J., John Wiley And Sons, Chichester.
- Wheater, H. S., Peach, D and Binley, A., 2007. Characterising groundwater-dominated lowland catchments: the UK Lowland Catchment Research Programme (LOCAR), *Hydrol. Earth Syst. Sci.* 11(1), 108-124.

Wriedt, G. and Rode, M., 2006. Modelling nitrate transport and turnover in a lowland catchment system, *J. Hydrol.* 328, pp157-176.

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Table 1: Census dates with associated relative proportions of dominant land uses and historical agricultural loadings as a proportion of current-day agricultural loadings

Agricultural census year	Grassland Area (%)	Cereal area (%)	Grassland agricultural input as proportion of current day loading	Cereal agricultural input as proportion of current day loading
1931	60	25	0.71	0.03
1969	32	60	1.27	0.51
1976	34	55	1.38	0.46
1981	30	62	1.30	0.72
1988	25	67	1.03	1.05
2000	31	64	1.00	1.00

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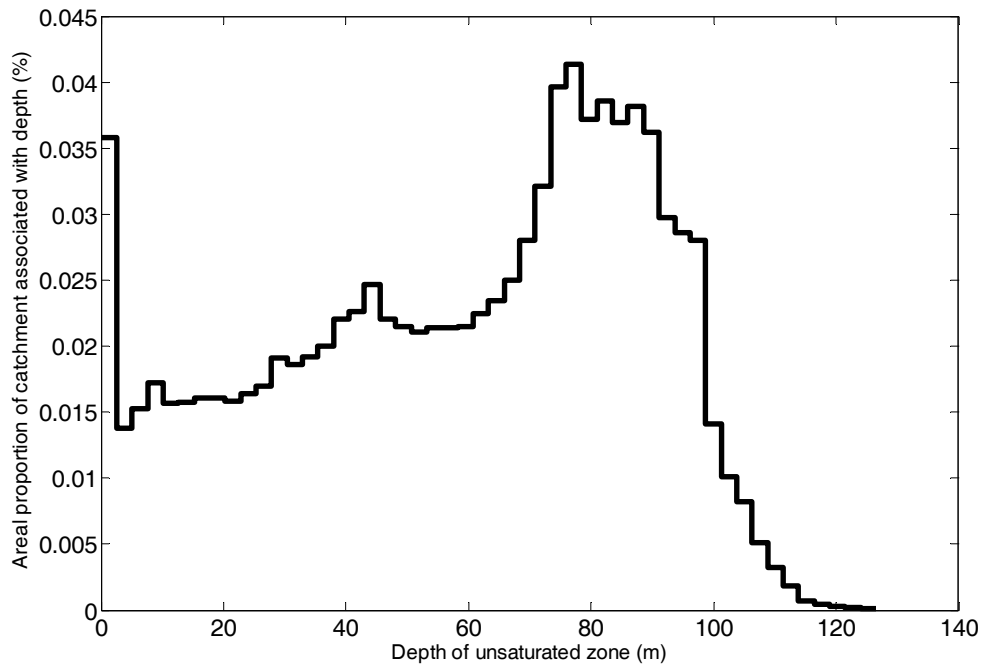


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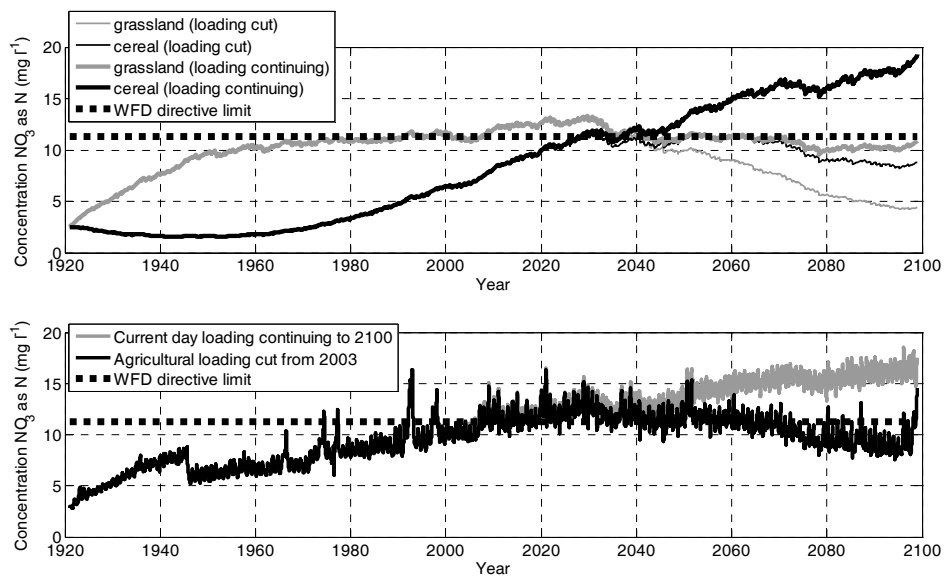


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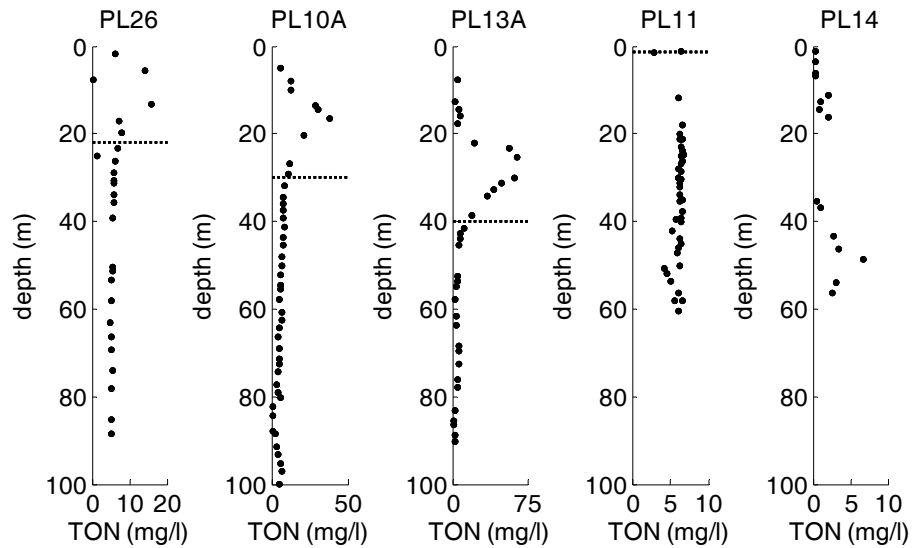


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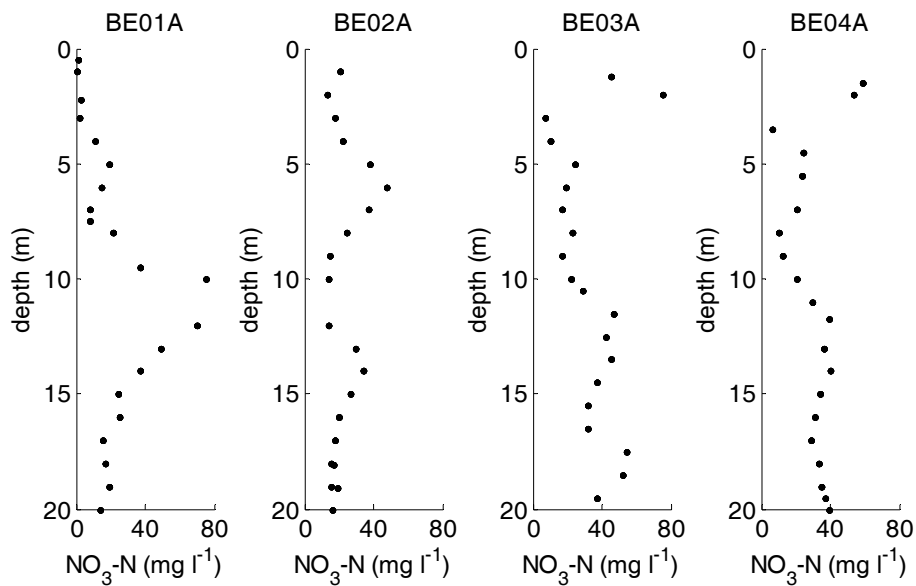


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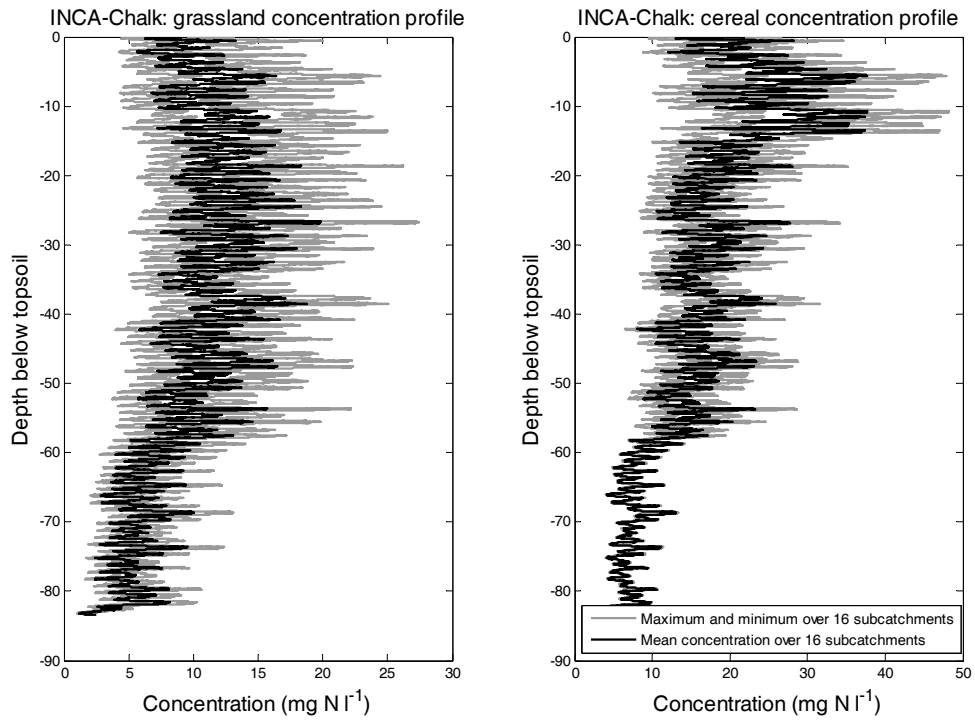


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